Differential Capacitance of Ionic Liquid Interface with Graphene: The Effects of Correlation and Finite Size of Ions

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Outline

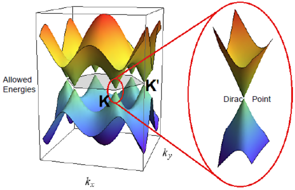
- Background and Motivation
- Ionic Liquids
- Graphene Electrodes
- Computational approach
- Results
- Conclusions and Future Work

Background and Motivation

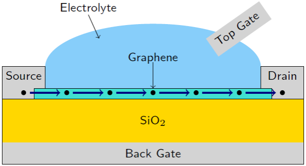
Graphene:

- High mobility of charge carriers in π electron bonds
- Zero-Energy band gap
- Dirac cone approximation
- Operate as field effective transistors

π Electron Energy Over Brillouin Zone



A.H. Castro Neto et al., Rev. Mod. Phys. 81 (2009) 109



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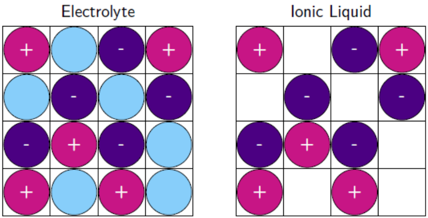
Ionic Liquids



- Melting points below 100 C
- Comprised strictly of positive and negative ions
- High conductivity and lower volatility than typical electrolytes
- Inter ionic correlations and overscreening

Free energy functional

Gibbs Free Energy:

$$F = U - TS$$

Functional for ionic liquids:

$$F = \int \left[-\frac{\varepsilon}{8\pi}\left(|\nabla\phi|^2 + l_c^2(\nabla^2\phi)^2\right) + \rho\phi - TS \right] d^3r$$

where the charge density ρ is defined as:

$$\rho = e(z_+c_+ - z_-c_-)$$

with the entropic term:

$$-TS = \frac{K_BT}{v}\left[vc_- \ln(vc_)) + vc_+ \ln(vc_+) + (1 - vc_- - vc_+)\ln(1 - vc_- - vc_+)\right]$$

Poisson Fermi equation

Minimization w.r.t the concentration yields:

$$c_{\pm} = \frac{c_{\infty} e^{\beta\phi}}{1-\gamma+\gamma\cosh\left(ze\beta\phi\right)}$$

where c_{∞} is the concentration in the neutral bulk, $\beta = \frac{1}{K_B T}$ and $\gamma = 2vc_{\infty}$ defines the ionic packing fraction

Minimization w.r.t the potential yields:

$$(1-\delta_c^2\nabla^2)\nabla^2\phi = -4\pi\rho$$

with $\delta_c = \frac{l_c}{\lambda_D}$ is a dimensionless correlation length with λ_D defining the Debye length in the ionic liquid

Differential Capacitance in the Diffuse Layer

Charge density per unit area:

$$\sigma_d(\phi_0) = \int_0^\infty \rho(\phi(x); \phi_0) dx$$

Apply external voltage to the bulk resulting in a potential drop across the diffuse layer:

$$V_d = -\phi_0$$

Differential capacitance per unit area:

$$C_d = \frac{d\sigma_d}{dV_d}$$

1D Problem

- Exploit the planar geometry to solve a 1D the modified Poisson Boltzmann equation:

$$\phi^{''} - \delta_c^2 \phi^{''''} = -4\pi\rho(\phi)$$

which the BCs:

$$\phi(0) = \phi_0, \phi(0)^{'''} = 0, \phi^{'}(\infty) = 0, \phi^{'''}(\infty) = 0$$

- Inclusion of Graphene requires non trivial changes to the Boundary conditions.
- Utilize the charge neutrality condition.

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Graphene electrode

Density of States:

$$D(\varepsilon) = \iint \frac{g}{(2\pi)^2}\delta(\varepsilon - \varepsilon(\vec{k}))d^2\vec{k}$$

which can be linearized by the Dirac Cone approximation to give:

$$D(\varepsilon) \approx \frac{2|\varepsilon|}{\pi(\hbar v_F)^2}$$

Charge Density on Graphene:

$$\sigma_g(\varepsilon_F) = -e\int D(\varepsilon)\left[\frac{1}{1+e^{\beta(\varepsilon-\varepsilon_F)}} - \frac{1}{1+e^{\beta\varepsilon}}\right]d\varepsilon$$

Then we define the differential capacitance per unit area i.e the quantum capacitance as:

$$C_g = -e\frac{d\sigma_g}{d\varepsilon_F}$$

which gives the following expression for C_g:

$$C_g = 2\Gamma_g \ln[2\cosh\frac{\beta e V_g}{2}]$$

where $\Gamma_g = \frac{2\alpha^2}{\pi e^2 \beta}$, with $\alpha = \frac{e^2}{\hbar v_F}$, $v_F \approx 10^6 m/s$ and $V_g = \mu_c/e$

The Neutrality Condition

Applied potential:

$$V_a = V_d + V_g$$

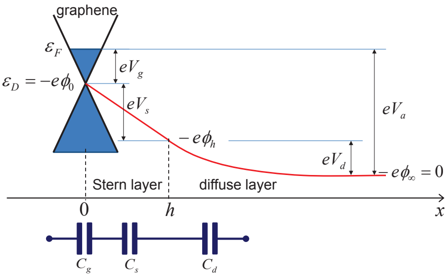
Charge neutrality condition:

$$\sigma_d(V_d) + \sigma_g(V_g) = 0$$

Therefore, we can impose the charge neutrality condition to find the relationship between V_d and V_g to find the total capacitance $C_{dg} = \frac{d\sigma_d}{dV_a}$ as:

$$C_{dg} = [C_d(V_d)^{-1} + C_g(V_g)^{-1}]^{-1}$$

Inclusion of a Stern Layer



$$V_s = \frac{\sigma_d}{C_s}$$

$$C_s = \epsilon_s/(4\pi h)$$

$$C_{dsg} = [C_d(V_d)^{-1} + C_s^{-1} + C_g(V_g)^{-1}]^{-1}$$

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Computational approach: Algorithm

- Solve the modified Poisson Fermi equation for an array of initial potential values ϕ_0
- For each ϕ_0 value we find $\rho(\phi(x);\phi_0)$
- Numerically integrate to obtain $\sigma_d(\phi_0) = \int \rho dx$
- Define $V_d \equiv -\phi_0$ and interpolate the set of V_d and σ_d values to obtain a numerical approximation of $\sigma_d(V_d)$
- Impose the charge neutrality condition $\sigma_d(V_d) + \sigma_g(V_g) = 0$ and solve for $V_d(V_a)$ and $V_g(V_a)$, using $V_a = V_d + V_s + V_g$
- Calculate C_d, C_s, C_g and C_{dsg} using the expressions derived for the capacitances.

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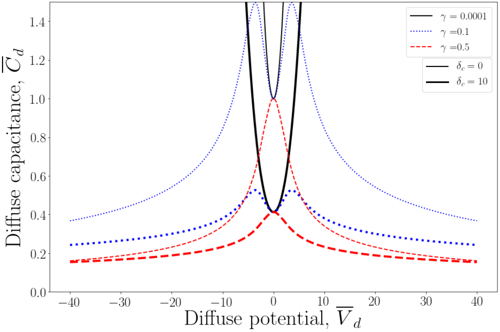
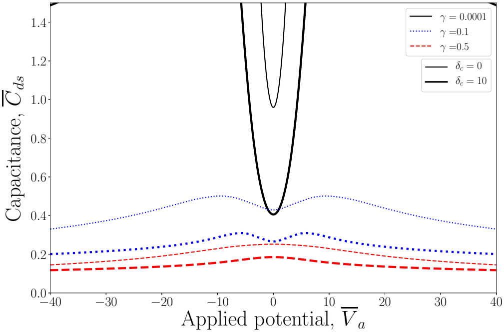
Diffuse Layer Capacitance C_d



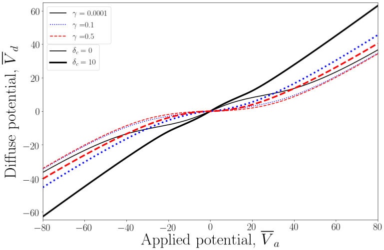
- Bell and camel shaped capacitances
- Ion correlations reduce the capacitance
- Independence of $\overline{C}_d$ from δ_c for large γ at large $|\overline{V}_d|$

Double Layer capacitance C_{ds}



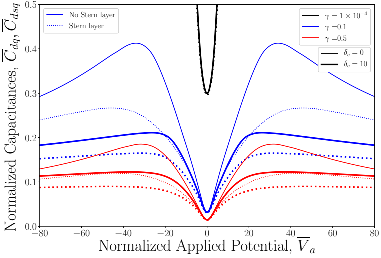
- Inclusion of Stern Layer lowers and broadens the capacitance peaks

Fraction of the total applied potential in diffuse layer, $V_a = V_d + V_g$



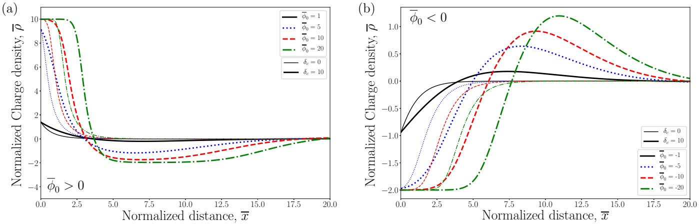
- Most of $\overline{V}_a$ goes to $\overline{V}_g$ i.e charging the graphene electrode
- $|\overline{V}_d|$ decreases with increasing γ and lowering δ_c
- ion correlations makes the differences for $\overline{V}_d$ for different γ more pronounced.

Total Capacitances, C_{dg} and C_{dsg}



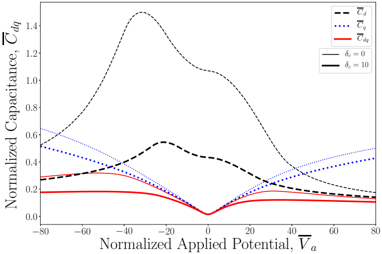
- $\overline{C}_g$ dominating the total capacitance around the PZC
- Broad peaks and camel shaped dependence for $|\overline{V}_a| >> 10$ for both $\gamma = 0.1$ and 0.5
- Stern Layer and ion correlations broaden the overall capacitance

Asymmetric Ionic Liquid: Charge density



- $\gamma_+ = 0.5$ and $\gamma_- = 0.1$
- Ion crowding effects $\overline{\rho} = \frac{1}{\gamma_\pm}$ and saturation for large $\overline{\phi}_0$
- interplay of screening and overcrowding effects for large $\overline{\phi}_0$

Asymmetric Ionic Liquid: Capacitances



- Asymmetry in $\overline{C}_d$
- $\overline{C}_q$ dominating around the PZC, V-shaped capacitance
- For $|\overline{V}_a| > 10$, asymmetric camel shaped $\overline{C}_{dq}$

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Concluding Remarks

- Ion packing fractions $\gamma = 0.1$ and $\gamma = 0.5$ give rise to camel and bell-shaped diffuse capacitances C_d respectively
- Inclusion of Stern layer reduces and broadens the peaks in capacitances
- Quantum capacitance C_g dominates around the PZC giving rise to camel shaped capacitances
- Asymmetric ionic liquids have asymmetric camel shaped capacitances as well due to C_g

Future Work

- Fully asymmetric ionic liquid electrolytes
  - Different valency
  - Different Correlation Lengths
- Explore New Boundary Conditions

Thank you for your attention

Asymmetric Ionic Liquids

Consider the case for an asymmetric ionic liquid with equal valency $z_- = z_+ = z$ but unequal ionic volumes v_-, v_+

$$c_+ = c_\infty \frac{e^{-ze\beta\phi}}{g(\phi)}$$

$$c_- = c_\infty \frac{e^{-ze\beta\phi} f(\phi)}{g(\phi)}$$

where $f(\phi)$ and $g(\phi)$ are given by:

$$f(\phi) = \left(1 + \frac{zv_- c_\infty}{1 - zv_- c_\infty (e^{ze\beta\phi} - 1)}\right)^{\frac{v_+}{v_-} - 1}$$

$$g(\phi) = f(\phi) + zv_+ c_\infty [e^{-ze\beta\phi} - f(\phi)] + zv_- c_\infty f(\phi)(e^{ez\beta\phi} - 1)$$